

## FABRICATION AND PROPERTIES OF ZIRCONIUM CERAMIC FROM ZIRCONIUM DIOXIDE NANOPOWDER

R. A. Lyubushkin,<sup>1</sup> V. V. Sirota,<sup>1</sup> and O. N. Ivanov<sup>1,2</sup>

Translated from *Steklo i Keramika*, No. 2, pp. 25 – 28, February, 2011.

A method of obtaining yttrium-stabilized zirconium ceramic by cold isostatic pressing without using a binder made from zirconium dioxide nanopowder obtained by reverse co-precipitation, is examined. X-ray structural, BET, and thermal analysis and transmission and atomic-layer microscopy are used to determine the main characteristics of the powder. It is determined that  $Zr_{0.92}Y_{0.08}O_2$  powder consists of a pure tetragonal phase with 10 nm particles. The microstructure and the composition of zirconium ceramic are studied by the TEM and XPA methods. The data obtained on the transition of the tetragonal phase of zirconium ceramic into the monoclinic phase with increasing sintering temperature are correlated with ceramic grain growth at high temperatures.

**Key words:** zirconium ceramic, zirconium dioxide, nanopowder, cold isostatic pressing.

It is well known [1] that ceramic materials based on zirconium dioxide  $ZrO_2$  possess an entire series of unique properties (high melting temperature, corrosion and chemical resistance, low thermal conductivity, quite high ionic conductivity, excellent biological compatibility, high mechanical strength and fracture viscosity, and so on), which determine the wide applications of such materials in the manufacture of high-strength structural and refractory articles, manufacture of fuel elements with oxide electrolytes, development of biocompatible ceramics, and so on.

The properties of zirconium ceramic can be varied substantially depending on the method used to synthesis the initial powder, determining the size, structure, and properties of the particles, the form of the modifying additives used to obtain ceramic, method used to consolidate the powder, the sintering temperature, and so on.

One promising method of modifying the properties of zirconium ceramic is using as the initial material zirconium dioxide nanopowder [2]. In this case one can expect optimization of the technological process of obtaining ceramic, due to a large decrease of the sintering temperature because of the high rate of diffusion of the nanopowder being sintered, and improvement of the properties of the ready ceramic article due to the formation of submicron fine structure of the material during sintering at low temperatures.

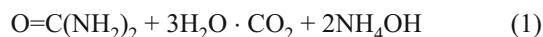
The objectives of the present work were as follows:

- synthesize of weakly agglomerated zirconium dioxide nanopowder, stabilized by yttrium, and comprehensive certification of the morphology, dispersity, and phase composition of the synthesized powder;

- investigate the formation of the structure and change of the phase composition during sintering of a ceramic material made from compacted synthesized nanopowder.

It is known [3] that nanopowders have a tendency to agglomerate, which complicates their use for developing ceramic and composite materials with uniform structure. For this reason, the production of non-agglomerated or slightly agglomerated nanopowders is an important technological problem.

In the present work, the method of chemical precipitation was chosen to synthesize yttrium-stabilized zirconium dioxide nanopowder (composition  $Zr_{0.92}Y_{0.08}O_2$ ); it is known [2] that yttrium oxide stabilizes at room temperature the tetragonal structure of zirconium dioxide, while at room temperature unstabilized zirconium dioxide crystallizes in the monoclinic modification). Zirconyl nitrate  $ZrO(NO_3)_2 \cdot 4H_2O$  and yttrium nitrate  $Y(NO_3)_3 \cdot 6H_2O$  with solution concentration 0.1 M were used as initial reagents. Urea was used as the main agent; on decomposition it forms *in situ*  $NH_4^+$  ions according to the reaction



and makes it possible to attain in solution pH values uniformly (no local jumps) which are necessary for precipitation.

<sup>1</sup> Belgorod State University, Community Center “Diagnostics of the Structure and Properties of Nanomaterials,” Belgorod, Russia.

<sup>2</sup> E-mail: Ivanov. Oleg@bsu.edu.ru.

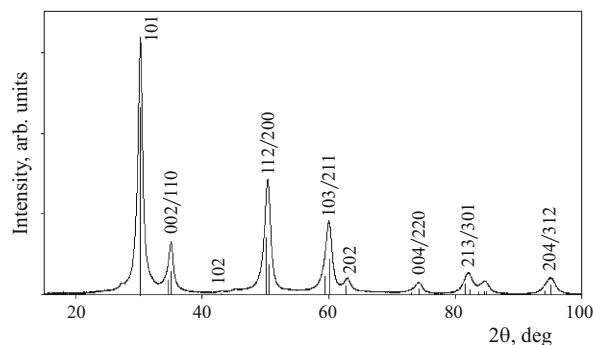


Fig. 1. Diffraction pattern of a  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  sample sintered at 500°C.

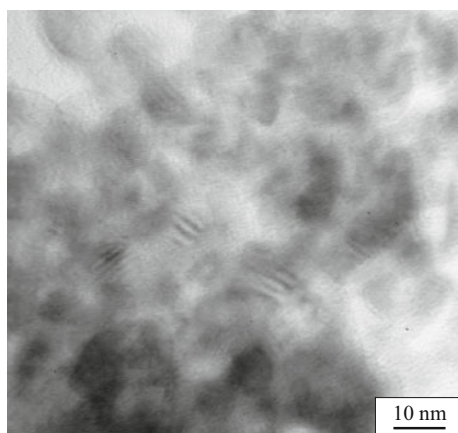


Fig. 2.  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  powder particles.

The hydrogel obtained was separated from the mother liquid, repeatedly washed with water and alcohol, and dried in air at 50°C in 48 h.

It was established that the synthesized powder is amorphous and heat-treatment at 500°C for 3 h in air is necessary for it to crystallize. The temperature 500°C was established on the basis of data from thermal analysis performed using the methods of differential-thermal analysis and differential scanning calorimetry using an SDT Q600 thermal analyzer. The specific surface area of the powder obtained, found by the BET absorption method (gas-adsorption analyzer TriStar II 3020), was 73 m<sup>2</sup>/g.

The phase composition and structure of the synthesized powder after sintering was determined by x-ray phase analysis (Rigaku Ultima IV diffractometer;  $\text{CuK}_\alpha$  radiation, Ni filter). The diffraction pattern of the powder is displayed in Fig. 1.

According to the ICDD card file, the material obtained is a single-phase solid solution  $\text{Zr}_{1-x}\text{Y}_x\text{O}_2$  and has a tetragonal crystal structure with space group  $P42/nmc$ . The lattice parameters were calculated from an analysis of the diffraction pattern:  $a = 3.5821 \text{ \AA}$ ,  $c = 5.2340 \text{ \AA}$ ; the degree of tetragonality was determined as  $c/a = 1.46$ .

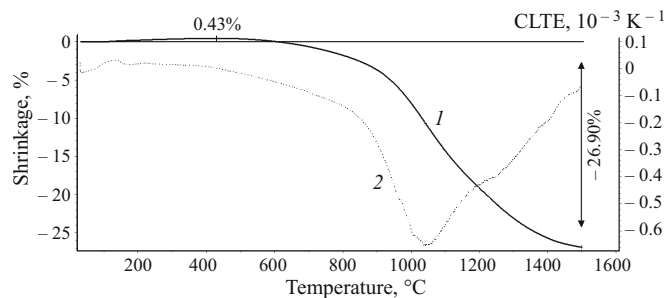


Fig. 3. Temperature dependence of the deformation (1) and CLTE (2) of a compacted sample.

An x-ray spectral analysis was performed with a Quanta 200 3D scanning ion-electron microscope to determine the precise elemental composition of the material. It was found that the composition of the material synthesized corresponds to the required composition  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$ .

Atomic force microscopy (AFM), which permits obtaining a three-dimensional image of dielectric materials, was used to determine the topographic and structural features of  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$ . The experiments were performed using a NTegra Aura scanning probe laboratory in the semicontact phase-contrast regime. The experiments established that  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  powder consists of elongated particles with irregular shape and average size about 10 nm in length, forming weakly bound agglomerates with average size about 100 nm.

The investigation of the  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  powder using a transmission electron microscope (TEM, JEM-2100 microscope) also showed that the powder consists of ellipsoidal particles with average size about 10 nm (Fig. 2), which agrees with AFM data.

$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  nanopowder was subsequently used as the initial material to obtain zirconium ceramic.

The  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  nanopowder was compacted by means of cold (at room temperature) isostatic pressing using an EPSI 400-200\*1000Y press under pressure 400 MPa. This pressing method yields high-density, mechanically strong, uniform blanks. The high uniformity of isostatically compacted blanks gives uniform sintering conditions in the entire volume of the material.

The material compacted from  $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$  nanopowder was sintered in air. The behavior of the compacted powder during firing was investigated by dilatometry (NETZSCH DIL 402 C dilatometer). The results of thermomechanical analysis at temperatures from 20 to 1500°C are shown in Fig. 3.

It was established that appreciable compaction of the compacted material already starts at about 650°C. The maximum rate of shrinkage is reached at 1040°C, i.e., the most intense sintering of the material occurs. A subsequent increase of the temperature leads to gradual slowing of the compaction of the material.

The XPA data also established the effect of the sintering temperature on the phase composition of the material

(Fig. 4). The maximum calcination temperatures were 980, 1200, 1500, and 1750°C with the same soaking time 5 h. An increase of the calcination temperature leads to the appearance in the sintered material of, aside from the initial tetragonal phase, a monoclinic phase with space group  $P121/c1$ , and as the sintering temperature increases the fraction of the monoclinic phase increases. Thus, for calcination at 980°C in air for 5 h the monoclinic phase fraction is 5% and at 1750°C — 93%.

The appearance of a monoclinic phase could be due to recrystallization of compacted material during sintering, resulting in larger grains in the material.

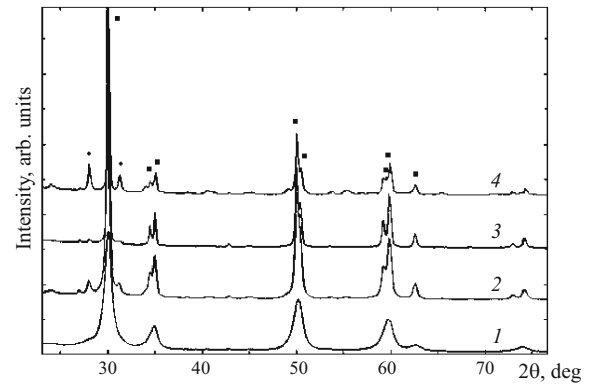
The monoclinic phase is characterized by larger crystallites than the tetragonal phase. For the standpoint of thermodynamics this means that there exists a positive driving force for transforming the tetragonal phase into the monoclinic phase, which arises from a change in the free-energy difference between the two phases. For this reason, in accordance with [4] we can write

$$D < D_{cr} = \frac{S}{[(G_t - G_m) + (E_t - E_m)]} \left( \frac{Y_m}{\rho_m} - \frac{Y_t}{\rho_t} \right), \quad (2)$$

where  $D$  is the running value of the size of a crystallite;  $D_{cr}$  is the critical size of a crystallite;  $G_t$  is the free energy of the matter with a tetragonal structure;  $G_m$  is the free energy of the matter with monoclinic structure;  $S$  is the specific surface area of the material;  $Y_t$  is the free surface energy of the matter with tetragonal structure;  $Y_m$  is the free surface energy of the matter with monoclinic structure;  $E_t$  is the deformation energy of matter with a tetragonal structure;  $E_m$  is the deformation energy of matter with monoclinic structure;  $\rho_t$  is the density of matter with tetragonal structure;  $\rho_m$  is the density of matter with monoclinic structure.

Thus, a crystallite with size larger than  $D_{cr}$  should transform into the monoclinic phase. The introduction of a stabilizing additive into the crystal lattice of zirconium dioxide can slow down but not stop this process.

Microscopic analysis, performed with a Quanta 2000 3D scanning electron microscope, did indeed show an in-



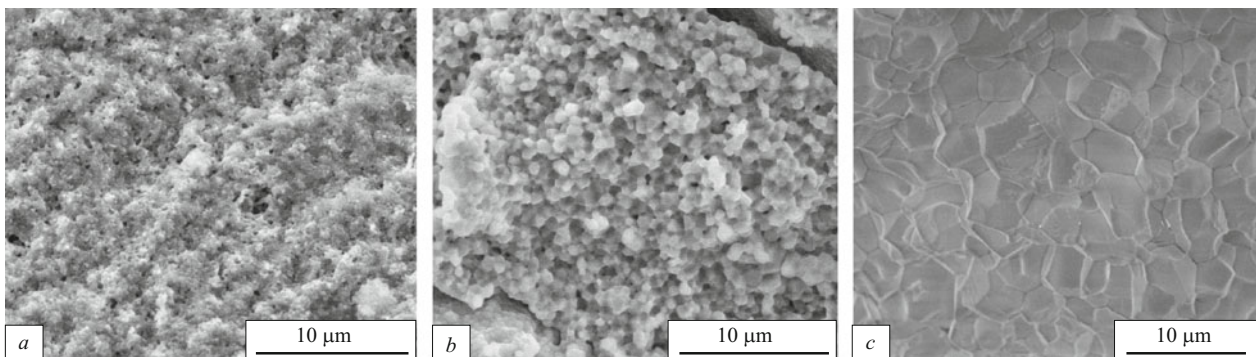
**Fig. 4.** Diffraction patterns of compacted material after sintering at different temperatures: 1) initial state; 2) 980°C; 3) 1200°C; 4) 1500°C; ■) tetragonal modification; ▼) monoclinic modification.

crease of the grain size of the zirconium ceramics studied. Thus, the average grain size in samples is about 150 nm after calcination for 5 h at 1200°C and about 570 nm at 1500°C.

Subsequent increases of the calcination temperature to 1750°C gives rise to the appearance in the ceramic of a marked grainy structure with grain size 1.74–5.1 μm (Fig. 5c) with a change of the grain shape from the initial rounded to polyhedral.

It should be noted that the changes noted in the phase composition and grain structure (grain size and shape) of zirconium ceramic correlate with the change of its microhardness  $HV$ . The results of the investigation of the Vickers hardness, measured with a 402 MVD Instron microhardness gauge, showed that the microhardness increases with sintering temperature as follows:  $HV = 10.1$  GPa at sintering temperature 1200°C, 11.5 GPa — at 1500°C and 12.4 GPa — at 1750°C.

*This work was performed as part of the government contract No. 02.740.11.0399 (Special Federal Program "Scientific and Scientific-Pedagogical Talent of Innovative Russia" for 2009–2013).*



**Fig. 5.** Microstructure of ceramic after sintering at different temperatures: a) 1200°C; b) 1500°C; c) 1750°C.

## REFERENCES

1. N. P. Lyakishev and M. I. Alymov, "Nanomaterials for construction," *Ross. Nanotekhnologii*, **1**(1–2), 71–81 (2006).
2. S. N. Kul'kov and S. P. Buyakova, "Phase composition and particulars of structure formation based on stabilized zirconium dioxide," *Ross. Nanotekhnologii*, No. 1–2, 119–132 (2007).
3. T. K. Gupta, F. F. Lange, and J. N. Bechtold, "Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase," *J. Mater. Sci.*, **13**(5), 1464–1470 (1978).
4. G. A. Gogotsi and A. V. Bashta, "Investigation of ceramics with penetration of a diamond Vickers pyramid," *Probl. Proch.*, No. 9, 49–54 (1990).